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Use of Organic Probes in Detecting Active Sites in Heterogeneous Catalysis[1]

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The inconsistencies encountered in the catalytic behavior of certain commercially available catalysts led us to study the nature of heterogeneous catalysts as a function of their preparation. One of the experiments carried out by students in our teaching laboratory consisted in the dehydration of cyclohexanol to cyclohexene over commercially available activated alumina. One shipment of the catalyst, however, with the same code number as the catalyst previously purchased from the same manufacturer, yielded methylcyclopentenes as the major product of dehydration. The two aluminas showed the same X-ray pattern and the same surface area. Since we were unable to obtain any information about the methods of preparation of the two batches of alumina, we decided to make a systematic study of the effect of preparation of aluminas on their catalytic activity. Subsequently, we expanded the study to include nickel and chromia catalysts.

1. ALUMINA

Two types of alumina catalyst were prepared (*1*).

Al_2O_3-A was prepared by means of hydrolysis of aluminum isopropoxide. The aluminum hydroxide thus obtained was dried and calcined.

Al_2O_3-B was made from potassium aluminate solution, obtained by dissolving aluminum shavings of 99.99% purity in aqueous potassium hydroxide. The bulk of the base was neutralized with nitric acid, and then a stream of carbon dioxide was bubbled through it. The precipitate was washed and dried at 110°C, compressed, and broken up to give 8- to 10-mesh particles.

Both Al_2O_3-A and -B were calcined to about 700°C. They both showed identical X-ray patterns, and had approximately the same surface area. Al_2O_3-A did not contain any alkali ions, while the potassium content in Al_2O_3-B was 0.08%.

In addition to alumina-A and -B alumina-I was prepared by impregnating alumina-A with alkali ions to a content equivalent to that of alumina-B.

a. Acid Sites

The small alkali content in alumina-B produced a significant inhibiting effect on its ability to skeletally isomerize cyclohexene. Catalyst-B, containing 0.08% K^+, was inert toward skeletal isomerization of cyclohexene, whereas in the presence of alumina-A 83% of cyclohexene was converted to methylcyclopentenes. Skeletal isomerization of this type proceeds by a cationic mechanism.

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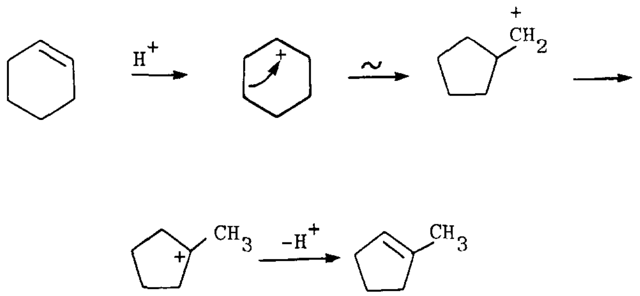
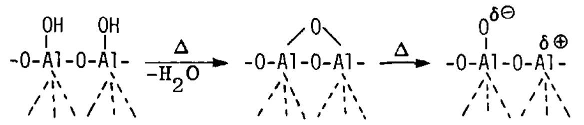


It can thus be concluded that alumina-A contains intrinsic acidic sites that catalyze the above isomerization.

The presence of acidic sites in aluminas can be explained by not fully coordinated aluminum atoms, and its formation during calcination could be pictured by the following model:

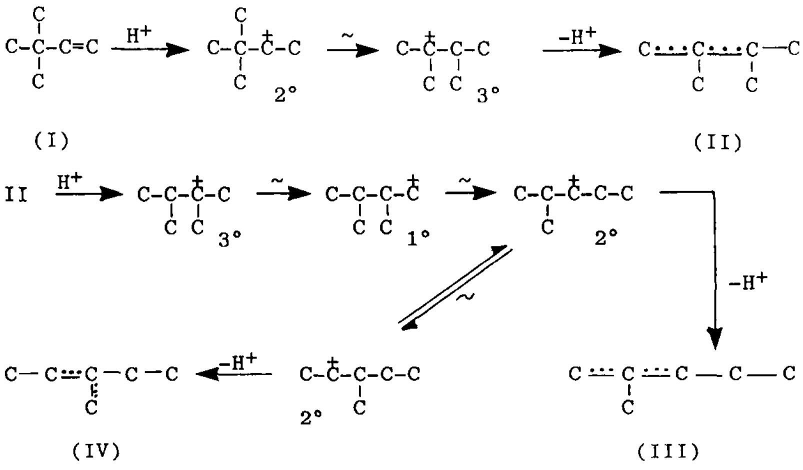


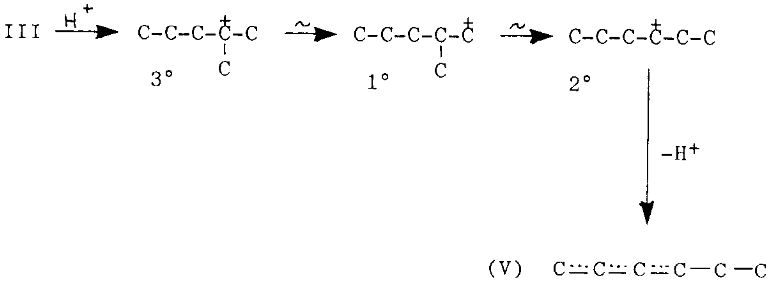
Adsorption of traces of moisture by the surface of the alumina deactivates Lewis acid sites, and generates Brønsted acidity.

The surface of an alumina catalyst is not uniform, and the strength of the acid sites can vary greatly. The kinetic study of the skeletal isomerization of 3,3-dimethylbutene served as a useful tool for the determination of the relative strengths of acid sites in aluminas, especially when the results were compared with those obtained from the skeletal isomerization of cyclohexene.

The isomerization of 3,3-dimethylbutene over Al_2O_3-A was performed at three different flow rates (Table 1) (*2*).

The data from Table 1 are plotted in Fig. 1 against the reciprocal space velocity as the time variable (*2*). They show that the first step in the reaction is the formation of 2,3-dimethylbutenes. These are then isomerized to 2- and 3-methylpentenes. The following cations appear to be involved in skeletal isomerization of 3,3-dimethylbutene:





The fastest reaction is the conversion of the starting olefin (**I**) to 2,3-dimethylbutenes (**II**), as the originally formed 2° cation is converted to the more stable 3° cation. The skeletal isomerization of **II** to **III** is more difficult and it requires stronger acidic sites because it involves the intermediate formation of the least stable 1° cation. Conversion of **III** to **IV** is a reversible reaction and occurs readily because only 2 and 3° cations participate in it.

The results of isomerization of 3,3-dimethylbutene and of cyclohexene over various aluminas are given in Table 2.

Alumina-A which is the most acidic of the three aluminas shows the highest conversion of cyclohexene to methylcyclopentenes and the lowest selectivity to the conversion of 3,3-dimethylbutene to 2,3-dimethylbutenes. Al_2O_3-B seems to have all the strong acidic sites neutralized as evidenced by the high selectivity factors, and by its inertness to the isomerization of cyclohexene.

Although alumina-B and -I contain the same concentration of K^+, their catalytic performance, as judged from the selectivity factor, indicates that in Al_2O_3-B all the strong acidic sites were neutralized, while in Al_2O_3-I the neutralization of acidic sites was not uniform; part of the strong acidic sites remained intact. The presence of strong acidic sites in Al_2O_3-I is also demonstrated by its ability to skeletally isomerize cyclohexene.

b. Base Sites

The model proposed for an alumina catalyst indicates that the surface of alumina contains not only acid but also base sites. The study of dehydration of alcohols had demonstrated the participation of base sites in this reaction.

Dehydration of cyclohexanol over alumi-

TABLE 1

Hexene Isomers Obtained from the Isomerization of 3,3-Dimethyl-1-butene over Alumina[a]

Expt.:	1	2	3	Equil.
HLSV[b]:	6.0	2.0	0.5	
Compound				
3,3-Dimethyl-1-butene	21.0	2.7	1.9	0.5
2,3-Dimethylbutenes	73.0	39.3	23.0	11.5
2-Methylpentenes	6.0	37.2	42.6	40.5
3-Methylpentenes	—	19.8	31.0	33.5
n-Hexenes	—	1.0	1.5	14.1

[a] Temp., 350°C.

[b] Hourly liquid space velocity = volume of liquid feed per volume of catalyst per hour.

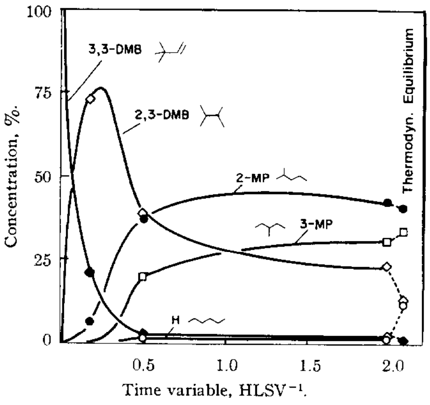
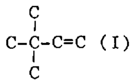


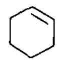
FIG. 1. Isomerization of 3,3-dimethyl-1-butene; product distribution as a function of the time variable.

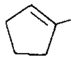
TABLE 2

Isomerization of 3,3-Dimethylbutene and of Cyclohexene over Various Aluminas

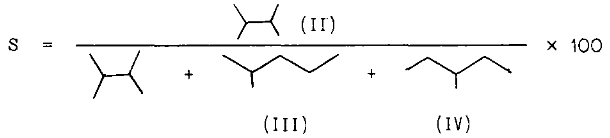


$C-\overset{C}{\underset{C}{C}}-C=C$ (I)



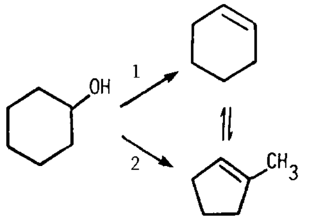
Al_2O_3	Conversion of I (%)	Composition of hexenes		Selectivity (S) (%)	 (%)
		II (%)	III + IV (%)		
A	97	39	57	40	43
B	76	73	2	97	0
I	87	56	23	65	32

Note.



A, ex $Al(i-OC_3H_7)_3$—by hydrolysis; 287 m^2/g. B, ex $KAlO_2$; 0.08% K^+; 254 m^2/g. I, by impregnation of A; 0.1% K^+; 280 m^2/g.

nas containing 0.4% of K^+ or Na^+ afforded cyclohexene as the only product (*3*). However, when cyclohexanol was passed over alumina-A, free of alkali ions, a mixture of cyclohexene and methylcyclopentenes was obtained. Two mechanistic pathways could be considered.



The product composition varies as a function of contact time (Fig. 2).

The fact that dehydration of cyclohexanol at short contact time is not accompanied by skeletal isomerization, indicates that the formation of cyclohexene does not occur via a cationic mechanism, and implies that both intrinsic acidic and basic sites must participate in the elimination of the elements of water. To test the latter hypothesis menthol and neomenthol were subjected to dehydration (Table 3) (*4*).

2-Menthene, although thermodynamically the least stable, is the preponderant

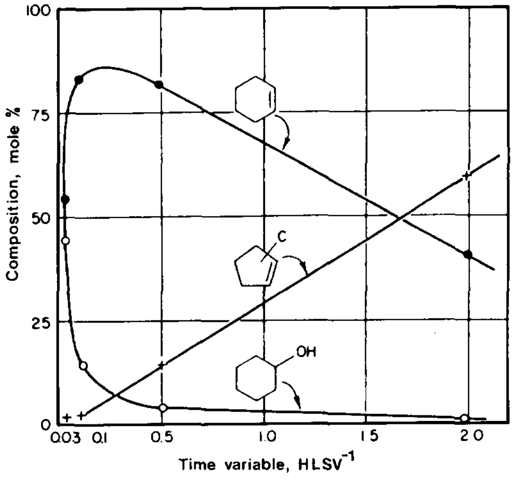
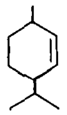
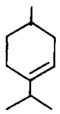
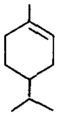
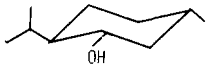
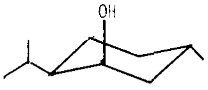


FIG. 2. Dehydration of cyclohexanol over alumina-A at 410°C. Influence of contact time.

TABLE 3

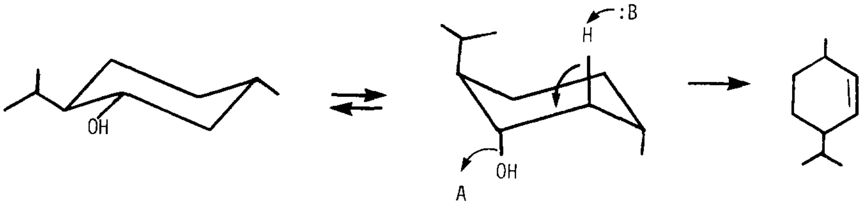
Composition of Menthenes from the Dehydration of Menthol and Neomenthol over Alumina at 290 to 330°C

	Composition (%)		
	 (2-Menthene)	 (3-Menthene)	 (1-Menthene)
 (Menthol)	→80–90	18–10	<2
 (Neomenthol)	→4–25	75–95	<1

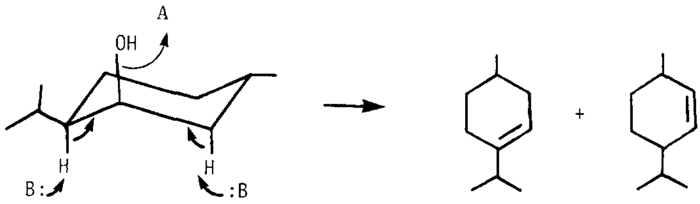
product of dehydration of menthol, which is a clear indication of a *trans* elimination of the elements of water. This is further supported by the results obtained from the dehydration of neomenthol which yields 3-menthene as the preferred compound.

The *trans* elimination can take place when the basic sites of the alumina attack the hydrogen from one side of the plane, and the hydroxyl group is removed from the opposite side of the plane by the acidic sites of the alumina.

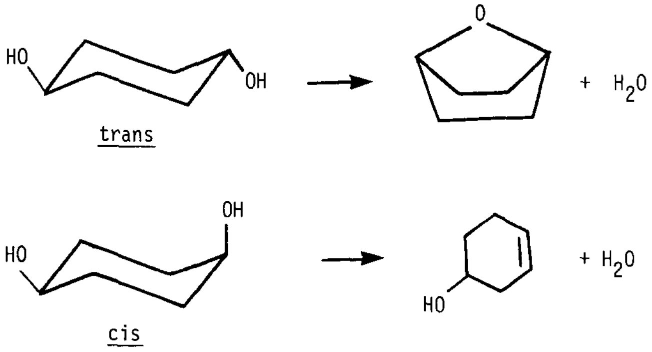
For menthol to undergo *trans* elimination it would be necessary for the original chair conformation with the hydroxyl in the more stable equatorial position to flip to another chair conformation with the hydroxyl in the axial position.



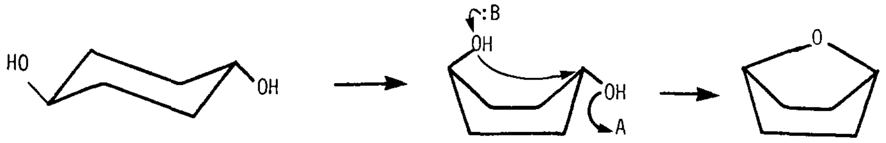
The *trans* elimination of neomenthol can produce 2- and 3-menthene, the latter being thermodynamically more favorable and the predominant isomer.



The reaction of *cis*- and *trans*-1,4-cyclohexanediol over alumina is another example of stereospecificity of the dehydration reaction, with the apparent participation of acid and base sites of alumina (*5*). The reaction which occurs at 256°C can be presented schematically as follows:

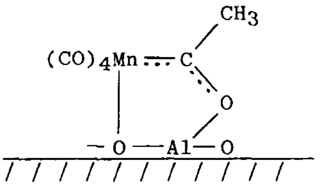


For the *trans*-diol to undergo dehydration, the chair conformation of the diol has to change to the boat form to give the right conformation for the attack:



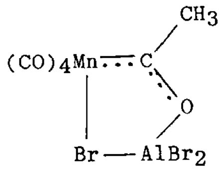
When basic sites of the alumina are neutralized with organic Lewis acids, such as tetracyanoethylene, dehydration does not occur.

Although the participation of Lewis basic sites of aluminas in catalytic dehydration reactions was proposed in the early 1960s, the evidence of their existence, however, on partially dehydroxylated aluminas was demonstrated unequivocally only recently (*6*). The ir spectrum of $Mn(CH_3)(CO)_5$ on alumina corresponds to structure **A** with the Al serving as a Lewis acid toward the acetyl oxygen, and O serving as a Lewis base toward the Mn atom.



A

The ir spectrum of **A** is very similar to that obtained from the interaction of $AlBr_3$ with $Mn(CH_3)(CO)_5$, the X-ray structure of which was established as corresponding to **B** (*7*):



B

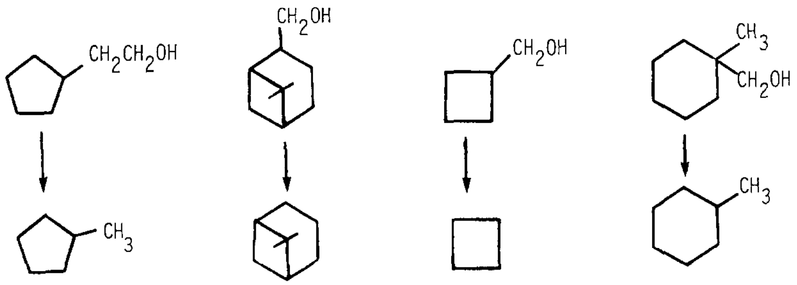
2. NICKEL

Studies of the effect of nickel catalysts, on saturated primary alcohols, have revealed that reduced nickel catalyst appears to contain contact catalytic sites responsible for hydrogenation–dehydrogenation reactions, and also weak acidic sites. The contact catalytic sites can be deactivated by the presence of sulfur-containing compounds, such as thiophene, alkylsulfides, etc., but at the same time the activity of the acid sites is greatly amplified. Sulfided nickel can thus act as an acid catalyst.

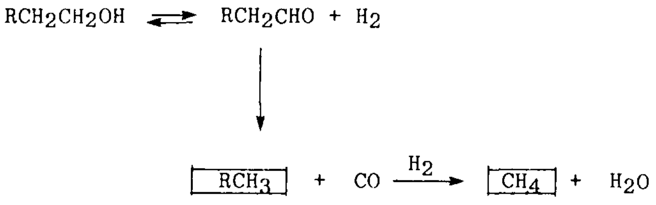
In a separate investigation it was observed that reduced nickel oxide, containing 1 to 2% of residual oxide, is an effective catalyst for the conversion of primary and secondary alkanols to the corresponding ethers. Further study indicated that the catalyst thus prepared contains both Lewis acid and base sites, and that both sites participate in the dehydration of alcohols to ethers.

a. Reductive Dehydroxymethylation of Primary Alcohols

Nickel catalysts such as those derived from the precipitation of nickel salts, Raney nickel, or commercially available nickel–kieselguhr, have been found to be effective catalysts for the reductive dehydroxymethylation of saturated primary alcohols (*8*):



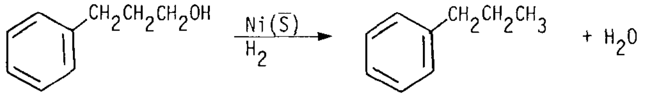
The reaction which is carried out under 5–20 atm of hydrogen pressure and at about 250°C, and with almost quantitative yield, can be presented as follows:

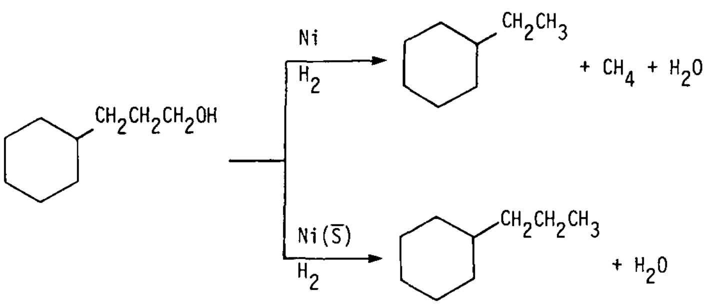


$$RCH_2CH_2OH \rightleftarrows RCH_2CHO + H_2$$
$$\downarrow$$
$$\boxed{RCH_3} + CO \xrightarrow{H_2} \boxed{CH_4} + H_2O$$

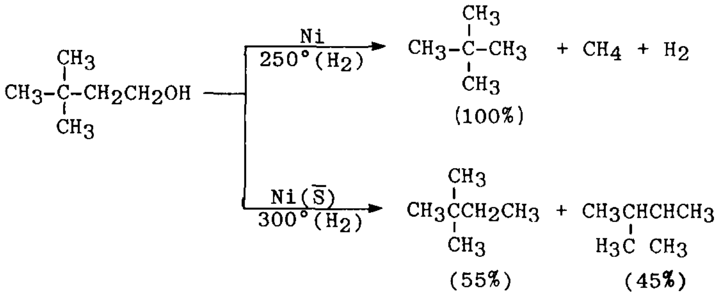
b. Effect of Sulfur Compounds

In order to apply this reaction to aromatic alcohols, with the prevention of hydrogenating the aromatic ring, it was deemed advisable to deactivate the catalyst with sulfur-containing compounds such as thiophene. It was found, however, that the presence of sulfur compounds modifies the nickel catalyst, and it becomes a reductive dehydroxylation catalyst:

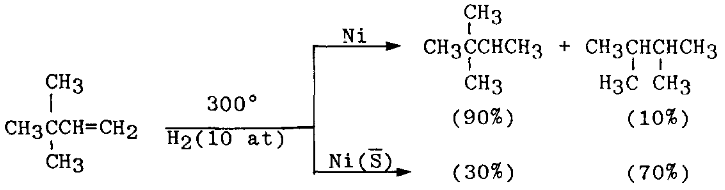




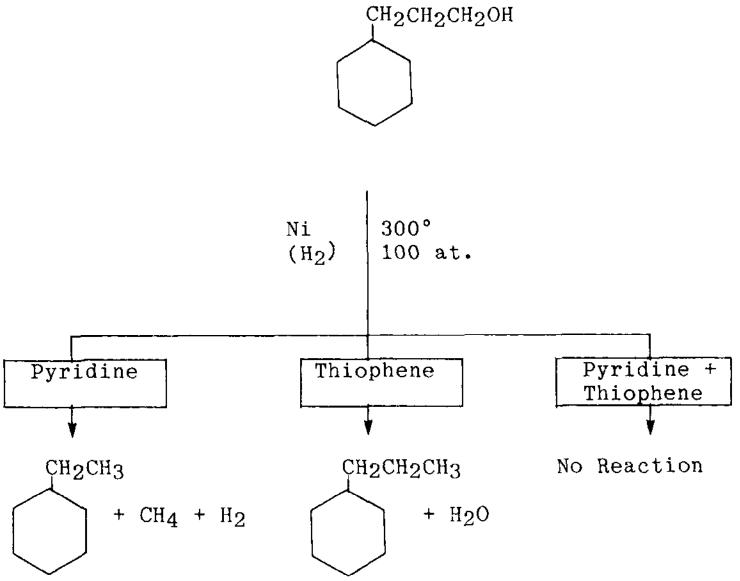
The presence of sulfur compounds imparts acidic properties to the nickel. This is demonstrated by skeletal isomerization that accompanies the hydrogenolysis of 3,3-dimethylbutanol with "sulfided" nickel catalyst:



Hydrogenation of 3,3-dimethylbutene in the presence of nickel and "sulfided" nickel catalysts had revealed that nickel per se may have mild intrinsic catalytic acidity, as indicated by the presence of small amounts of 2,3-dimethylbutane in the reaction product. However, with sulfided nickel, 2,3-dimethylbutane is the preponderant hydrocarbon.



From the above results it could be concluded that sulfur-containing componds deactivate the contact catalytic sites of the nickel, but leave the intrinsic acidic sites unimpaired. In conformity with the above hypothesis it was found that in the presence of pyridine, which neutralizes the acidic sites, and of thiophene, which deactivates contact catalytic sites, both reductive dehydroxymethylation and dehydroxylation reactions are inhibited:



"Sulfided" nickel acts as an acid catalyst in hydrocarbon conversion reactions. It was found that, in the presence of thiophene and hydrogen, under initial pressure of 5 to 8 atm, nickel catalyzes alkylation of toluene, and transalkylation of *tert*-butylbenzene (*9*). At 350°C about 35% of isobutylene charged reacted with toluene to form *m*- and *p*-*tert*-butyltoluene. In the absence of thiophene the yield of *tert*-butyltoluene was less than 4%.

Owing to its acidic properties, sulfided nickel deposited on silica–alumina catalyst is used in hydrocracking of higher hydrocarbons (*10*).

c. Participation of Base Sites and Acid Sites

When primary alkanols and hydrogen are passed over reduced nickel oxide catalysts at atmospheric pressure and at temperatures of 167 to 240°C the alcohols are converted to ethers (*11*):

$$\mathrm{RCH_2OH} \xrightarrow[(\mathrm{H_2})]{\mathrm{Ni}} \mathrm{(RCH_2)_2O + H_2O}.$$

The activity of the catalyst toward formation of ethers depends on the nickel oxide content of the reduced catalyst. Using neopentyl alcohol as the substrate and 170°C as the temperature of reaction, it was found that NiO content of 1.2 to 2.2% gives optimum selectivity for dineopentyl ether formation (Fig. 3) (*12*). At higher oxide content trimethylacetaldehyde is the principal product, while with a lower oxide content reductive dehydroxymethylation with the production of isobutane becomes the main reaction.

Since the conversion of alcohols to

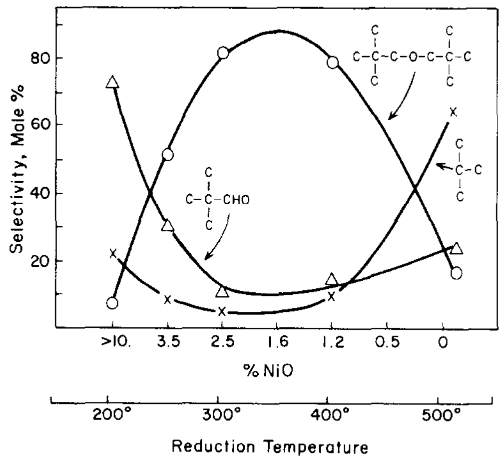


FIG. 3. Effect of nickel oxide content on the selectivity of ether formation.

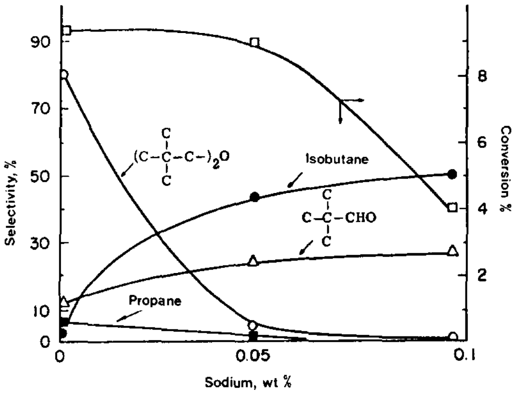


FIG. 4. Effect of sodium on reaction of neopentyl alcohol. Catalyst, Ni; temp., 195°C.

TABLE 4

Effect of Sodium on the Reaction of *n*-Butanol over 5% Nickel/CAB-O-Sil[a]

	Sodium (%)			
	0	0.1	0.5	1.0
Conversion (%)	28.5	28.5	17.1	2.9
Product (mole%)				
Dibutyl ether	91.6	85.1	56.9	24.2
Butyraldehyde	0.5	0.6	1.2	3.1
Propane	7.9	13.3	42.8	72.6

[a] Temp., 160°; H_2/C_4H_9OH = 4.6/1.0; HLSV, ~1.0.

ethers is usually associated with acidic sites, the effect of sodium on the reactivity and selectivity of reduced nickel oxide catalyst was investigated. For that purpose precipitated nickel hydroxide was impregnated with sodium hydroxide, calcined, and reduced *in situ* to obtain a catalyst containing 0.05 and 0.6% by weight of sodium (Fig. 4).

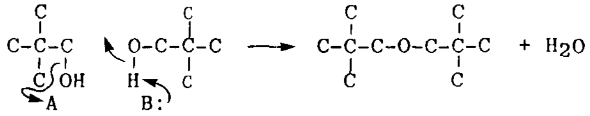
With sodium-free catalyst the main reaction product was ether, amounting to 80% of the reacted alcohol. However, in the presence of nickel, containing 0.05% of Na^+, the yield of ether dropped to less than 8%, the main reaction being reductive dehydroxymethylation and aldehyde formation.

Catalysts prepared from nickel oxide deposited on kieselguhr or Cab-O-Sil (silica), and containing 6–10% of nickel, gave results similar to that of the unsupported nickel catalyst. The presence of Na^+ in the catalyst inhibits the formation of ethers, while the dehydroxymethylation reaction increases.

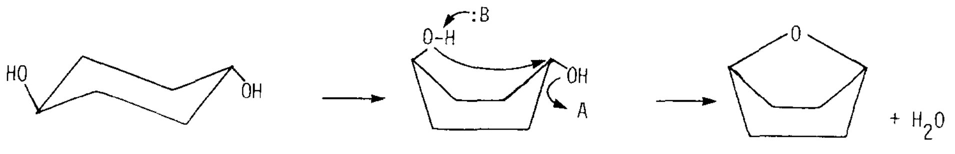
A continuous flow reaction at 190°C demonstrates that nickel–kieselguhr catalyst shows no deterioration after more than 16 h of use. At 170°C, with a hydrogen-to-alcohol ratio of 10 and HLSV of 1.0, 1-butanol reacted to the extent of 89%, with a yield of 91% of di-*n*-butyl ether.

However, the presence of Na^+ in supported nickel catalyst affects the reactivity of ether formation from *n*-butanol (Table 4) (*13*).

The inhibition of ether formation by sodium ions is an indication that intrinsic acidic sites of the nickel catalyst participate in the reaction. The reaction, however, does not proceed via a cationic mechanism, because neopentyl cation once produced would have undergone skeletal isomerization. It can thus be concluded that ether is formed by a cooperative action of intrinsic acidic and basic sites of nickel oxide:



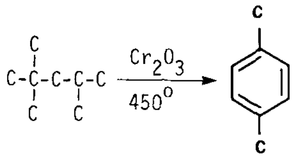
This type of biphilic participation is similar to that encountered in aluminas as described in the first part of this article. In order to demonstrate more convincingly that the formation of ethers proceeds by the involvement of both acidic and basic sites of the nickel catalyst, an experiment with *cis*- and *trans*-1,4-cyclohexanediol was performed (*14*). The diols were injected into a pulse reactor over 150- to 200-mesh-size 6% Ni–kieselguhr catalyst using hydrogen as a carrier gas. The product obtained from the *cis*-diol contained 5% 1,4-epoxycyclohexane, and from the *trans*-diol the content of the epoxy compound was 20%. The preferential formation fo 1,4-epoxycyclohexane from *trans*-diol is additional evidence that the elimination of the elements of water proceeds via a *trans*-elimination reaction requiring the participation of intrinsic acidic and basic sites on the catalyst.

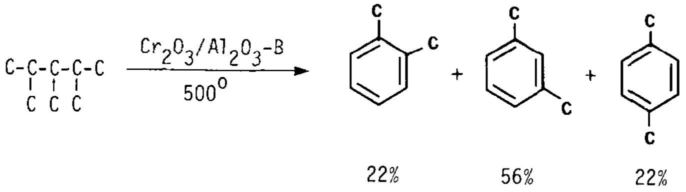


The small amount of epoxycyclohexane which is formed from the *cis* isomer can be attributed to the catalytic epimerization of the *cis*-diol to the *trans*-diol. The epimerization reaction can be greatly reduced by carrying out the experiment under 15 atm of hydrogen pressure, instead of the usual atmospheric pressure.

3. CHROMIA

Catalytic aromatization of alkanes in the presence of chromia is one of the most fascinating hydrocarbon conversion reactions. The mechanism of this reaction was reviewed in 1965 (*15*), and discussed further in 1981 (*16*). Aromatization of 2,2,4-trimethylpentane over chromia yields *p*-xylene, while that of 2,3,4-trimethylpentane over chromia deposited on "non-acidic" alumina produces a mixture of xylenes.



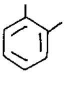
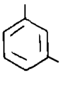
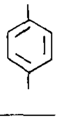
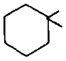
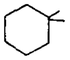
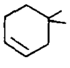
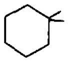


The xylenes once produced do not isomerize when passed over the above catalysts. Skeletal isomerization accompanying aromatization cannot thus be ascribed to a cationic reaction.

The nature of alumina used as a support for chromia has a significant effect on the course of dehydrogenation. Alumina-A, prepared from aluminum isopropoxide, causes skeletal isomerization of 1,1-dimethylcyclohexane or of its olefin. However, alumina-B, containing small amounts

TABLE 5

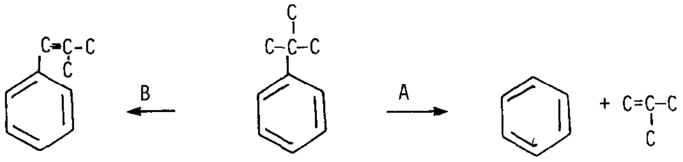
Effect of Aluminas on Dehydrogenation of 1,1-Dimethylcyclohexane and 3,3-Dimethylcyclohexene in the Presence of Chromia–Alumina Catalysts[a]

Al_2O_3	Hydrocarbon charged	Products formed				
		Aromatics (%)	Composition of aromatics (%)			
						
A		93	47	46	1	
B		98	98			
A		94	15	41	35	
B		96	98			

[a] Temp., 500°C; HLSV, 0.9.

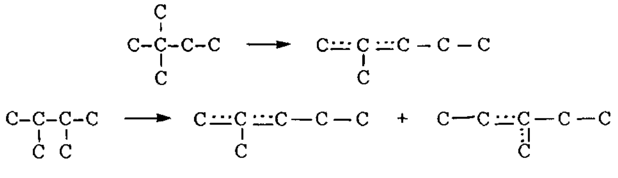
of alkali ions, converts the hydrocarbons to toluene almost exlusively (Table 5) (*17*).

Different products were obtained when *tert*-butylbenzene was passed over chromia deposited on alumina-A and alumina-B (*18*):

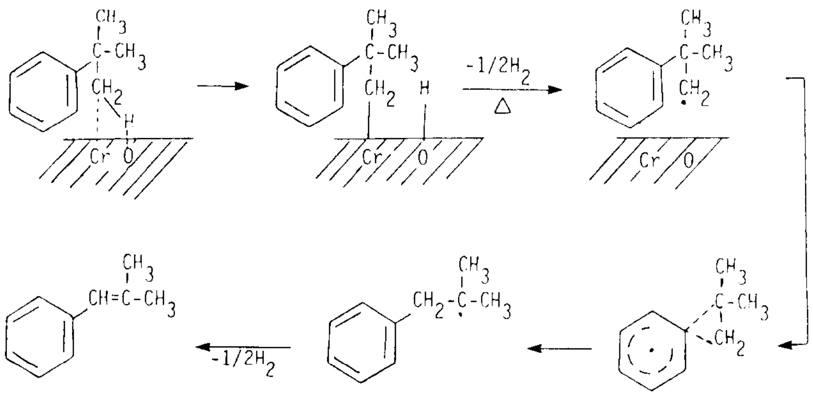


Over catalyst-A dealkylation resulted, while over the "nonacidic" catalyst-B, a product of skeletal isomerization was formed. The dealkylation is a cationic reaction, whereas the skeletal isomerization over a catalyst must be a non-acid-type rearrangement.

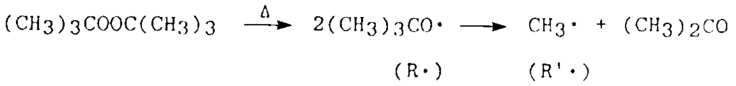
It is of interest to note that alkanes, such as neopentane and tetramethylbutane, which cannot undergo a direct dehydrogenation reaction to form alkenes, do not undergo skeletal isomerization when passed over chromia–alumina-B. On the other hand, 2,2-dimethylbutane undergoes both dehydrogenation and skeletal isomerization to 2-methylbutenes, and 2,3-dimethylbutane is converted to 2- and 3-methylpentenes.



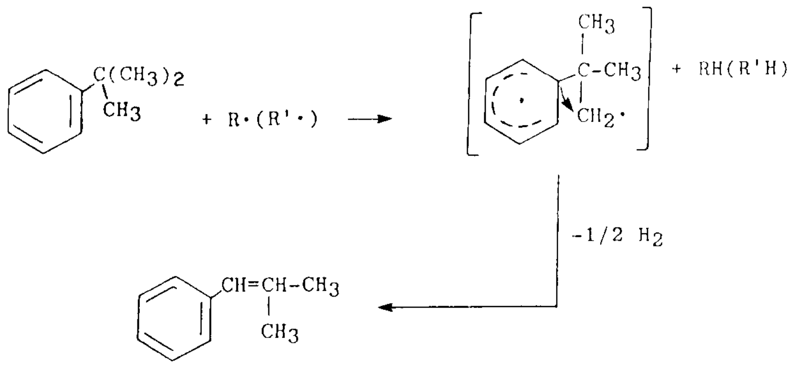
The skeletal isomerization of *tert*-butylbenzene to butenylbenzenes can be explained by a free-radical reaction, if we assume that a sigma bond formed between a carbon and chromium ruptures homolytically:



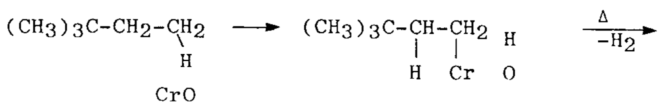
That skeletal isomerization of *tert*-butylbenzene to isobutylbenzene can occur by a free-radical reaction was demonstrated by heating *tert*-butylbenzene at 160°C in the presence of di-*tert*-butylperoxide, a free-radical initiator (*19*). The reaction can be presented as follows:



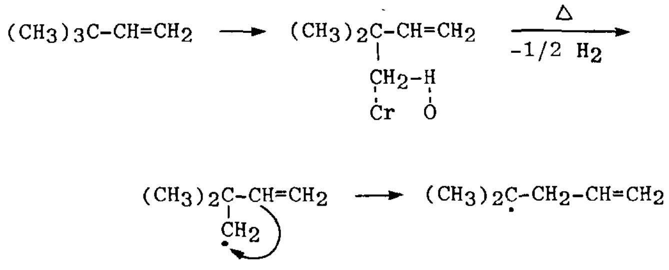
$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\Delta} \underset{(R\cdot)}{2(CH_3)_3CO\cdot} \longrightarrow \underset{(R'\cdot)}{CH_3\cdot} + (CH_3)_2CO$$



A free-radical mechanism involving vinyl migration can be applied to explain skeletal isomerization accompanying dehydrogenation of 2,2-dimethylbutane in the presence of nonacidic chromia–alumina catalyst (*20*).

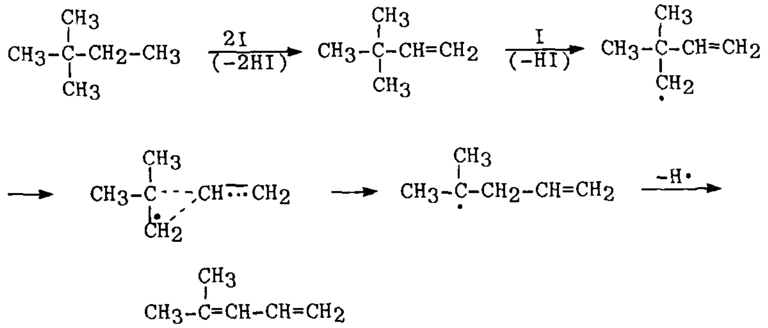


$$(CH_3)_3C\text{-}CH_2\text{-}\underset{\underset{CrO}{H}}{CH_2} \longrightarrow (CH_3)_3C\text{-}\underset{H}{CH}\text{-}\underset{Cr}{CH_2}\ \underset{O}{H} \xrightarrow[-H_2]{\Delta}$$

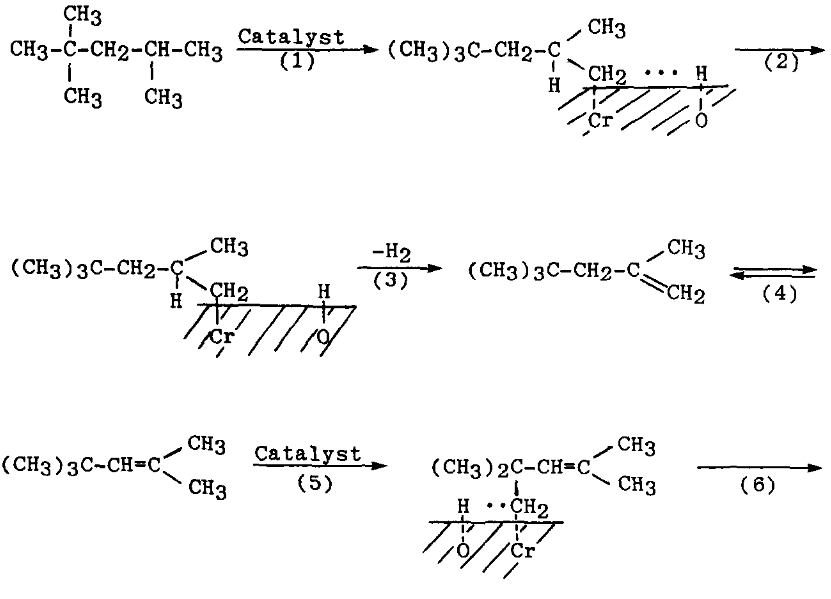


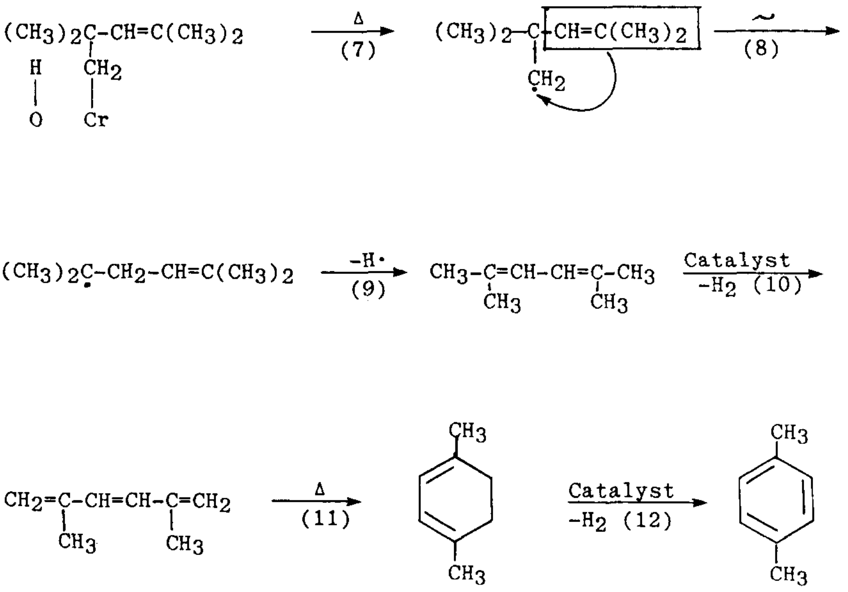
The hexenyl radical thus formed can be converted to a alkadiene or alkene, depending on whether it donates or absorbs a hydrogen atom.

A similar type of free-radical skeletal isomerization was reported to occur when 2,2-dimethylbutane was heated with iodine or hydrogen iodide (*21*):



The formation of *p*-xylene from 2,2,4-trimethylpentane can thus be explained by a combination of catalytic, free-radical, and thermal reactions:





Steps (1)–(4), (10), and (12), involve catalytic dehydrogenation of hydrocarbons over chromia. The homolytic rupture of the organometallic bond in step (7) is followed in step (8) by vinyl migration, similar to a free-radical reaction induced by iodine.

Step (11) is a thermal reaction not requiring a catalyst.

It can thus be concluded that the unique behavior of chromia catalysts in hydrocarbon conversion reaction can be attributed to a homolytic cleavage of the organometallic bond formed between chromium and the carbon atom of the hydrocarbon. The free radical thus produced may induce vinyl or phenyl migration, through the overlap of electrons between the unpaired electron and the multiple bond of the hydrocarbon moiety. The similarity of chromia-catalyzed hydrocarbon reactions and those induced by radicals gives further support to a free-radical involvement in chromia-catalyzed skeletal rearrangement of hydrocarbons.

On the basis of the numerous examples cited in the above presentation it can be asserted that judiciously chosen organic probes can serve as effective tools for detecting and evaluating active sites in heterogeneous catalysts.

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